Low threading dislocation density Ge growth and heavy phosphorus doping in Ge

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Heteroepitaxial growth of Ge on Si has generated great interest for different applications such as optoelectronic devices [1] and novel CMOS technologies [2]. Low threading dislocation density (TDD) is required to prevent degradation of electrical properties of devices, such as dark current of optical detectors. Deposition of Ge on virtual substrate is widely investigated using different approaches to reduce TDD [3-5]. Additionally, N doping such as phosphorus in Ge have been widely investigated because of potential to change Ge to direct band gap material by filling electron into L-valley. In this report, we demonstrate low threading dislocation density Ge growth by combination of cyclic annealing and etching. The heavy P doping in Ge by atomic-layer doping (P-ALD) approach is also discussed.

Epitaxial growth of Ge is carried out using a single wafer reduced pressure CVD system. After HF last clean, the wafer is baked at 850-1000°C and cooled down to 600°C in H₂ and further cooled down to 300°C in N₂ to form hydrogen-free Si surface. Then thin 2-demensional Ge seed layer (~50 nm) is deposited at 300°C using GeH₄ in N₂ carrier gas. After that the 2nd Ge layer is deposited at 550°C with H₂-GeH₄ gas mixture. For TDD reduction, cyclic annealing [5] in H₂ is performed during the Ge growth. After the deposition, the Ge layers of some samples are etched back by HCl in the CVD reactor for thinning. For the P-ALD experiment, the Ge surface is exposed to PH₃ with N₂ carrier gas. The exposure temperature is varied between 100-300°C. In order to investigate the effect of hydrogen-termination of the Ge surface, some wafers are cooled down in H₂ environment after the Ge layer growth is continued with N₂-GeH₄ gas mixture. P dose and profile are measured by SIMS. Active P dose is determined by Hall measurement at 10 K.

TDD as a function of blanket Ge thickness is shown in Fig. 1. In the case of the Ge growth with cyclic annealing (\circ), TDD is decreasing with increasing Ge thickness and $\sim 7 \times 10^5$ cm⁻² is achieved for 4.7 µm thick Ge [5]. By 4.5 µm thick Ge deposition and etching process (\Box), the level of the TDD is lower compared to the TDD of Ge layer of same thickness deposited by cyclic annealing process. For example TDD is reduced to $\sim 1.3 \times 10^6$ cm⁻² for a sample which was thinned to 1.8 µm, which is around one order of magnitude lower compared to deposited samples without etching. If the layer is thinned further the TDD is increasing, but is still lower compared to TDD measured for the Ge layers obtained by deposition only.

AFM images of blanket Ge surface before (4.5 μ m) and after etching (1.8 μ m) are shown in Fig. 2. By etching, cross hatch pattern becomes slightly smeared, but the surface roughness is not increased. Further etching was increasing the surface roughness.

In order to discuss impact of hydrogen-termination on Ge surface, P dose as function of PH₃ exposure temperature is shown in Fig. 3. During the cooling, N₂ or H₂ is chosen as carrier gas. In the case of the sample cooled down in H₂, very few P is adsorbed on the Ge surface at 100°C. With increasing PH₃ exposure temperature adsorbed P dose is increased. On the other hand, in the case of the sample cooled down in N₂, $\sim 8 \times 10^{13}$ cm⁻² of P is adsorbed even at 100°C. In this case, temperature dependence of P dose is small. At 300°C, no clear difference between N₂ and H₂ cooling is observed. These results indicate that the P adsorption is suppressed by hydrogen-termination of the Ge surface in the case of cooling down in H₂. The hydrogen desorption from the Ge surface starts from ~200°C resolving the surface passivation [6].

In Fig. 4, P dose as function of PH₃ exposure time at various PH₃ partial pressures is shown.

The PH₃ exposure is performed at 300°C on hydrogen-free Ge surface. For all PH₃ partial pressure used, P dose is increasing with increasing PH₃ exposure time and saturated at $\sim 1.5 \times 10^{14}$ cm⁻², which value is close to a quarter of monolayer of Ge (100). The saturation value does not depend on PH₃ partial pressure. The incorporated P dose Q_r on the hydrogen-free Ge surface can be described by Langmuir type kinetic.

$$Q_r = N_t \left[1 - exp \left\{ -k_r \left(\frac{KP_{PH3}}{(1 + KP_{PH3})} \right) \right\} \right]$$
(1)

Where N_t is saturation value of incorporated P dose, k_r and K are reaction rate and thermal equilibrium constants of PH₃ adsorbed on the Ge surface, respectively. Good agreement to Langmuir type adsorption model is obtained with $N_t=1.55\times10^{14}$ cm⁻² (a quarter of monolayer), $k_r=77$ s⁻¹ and $K=3.0\times10^{-2}$ Pa⁻¹.

References

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Ge Thickness (µm)

Fig. 1. TDD as function of Ge thickness. Blanket Ge is deposited. (\circ) shows the Ge sample deposited by cyclic annealing process and (\Box) shows the sample with Ge deposition (4.5 µm) and etching.



Fig. 3. P dose as function of PH₃ exposure temperature. N_2 (\Box) or H₂ (\circ) is used during temperature change before PH₃ exposure. PH₃ exposure time is 480 sec.



Fig. 2. AFM images of the sample after blanket Ge growth with cyclic annealing (a) and followed by etching (b). Ge thicknesses are (a) 4.5 μ m and (b) 1.8 μ m, respectively. [110] directions are shown by arrows.



Fig. 4. P dose as function of PH₃ exposure time. PH₃ partial pressure is varied. Dash lines are calculated by using equation (1) with N_t =1.55×10¹⁴ cm⁻², k_r =77 s⁻¹ and K= 3.0×10⁻² Pa⁻¹.